

ASSESSMENT OF THE FLAMGARD RETARDANT EFFICIENCY DURING THE THERMAL LOADING OF SPRUCE WOOD (*Picea abies* L.)

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ABSTRACT

The aim of the paper was to determine the resistance of spruce wood (*Picea abies* L.) treated with a flame retardant Flamgard after exposure of its surface to radiant heat. Treated samples were thermally loaded for 30 and 45 minutes and untreated sample were loaded for 30 minutes. The changes in the chemical composition of wood (extractives, lignin, cellulose and hemicelluloses content) in two layers which were removed below the charred layer (layer 1 - thickness up to 20 mm and layer 2 - thickness from 20 to 40 mm) and thickness of the charred layer were evaluated. During the thermal loading of a control sample, the temperature of 300°C in time of 920 seconds was observed. The average thickness of charred layer was 15.41 mm. The limit temperature of 300°C was not reached by both treated samples loaded for 30 and 45 minutes. The average thickness of charred layer of the treated samples was 10.03 mm (30 min.) and 20.04 mm (45 min.). The major chemical changes were recorded in the wood sample untreated with a retardant, mainly in the layer 1 (decrease in lignin by 12.26% and holocellulose content by 16.87%). The experiment showed that the retardant used reduced considerably the degradation of material in terms of changes in its chemical composition. There were no big changes of both lignin and holocellulose content during the thermal loading of the treated samples (decrease in lignin from 1.89 to 6.46% and holocellulose amount from 0 to 4.14%). The experiments also confirmed that the least thermally stable components of wood, namely hemicelluloses, were degraded to the greatest extent, most in the layer 1 of the control sample (decrease in 20.25 %).

Key words: spruce wood, flame retardant, thermal degradation of wood, extractives, cellulose, hemicelluloses, lignin

INTRODUCTION

Nowadays, we cannot imagine the building industry without wood. Spruce wood is the most commonly used in the building industry from among the various tree species. It represents a quality and also economically available raw material. This is mainly due to the tree composition of our forests. Spruce is one of the dominated coniferous tree species at our territory for several centuries.

However, wood is combustible material, which is on one hand positive property but also negative property of wood. Fire as undesirable burning is the main negative consequence of wood combustibility. (MAKOVICKÁ OSVALDOVÁ 2009). Burning can be divided into several phases. The most often used is the division into phases according to

temperature-time curve, based on which following basic phases are recognised: ignition, propagation, flashover, fully developed fire, and extinction (KARLSSON, QUINTIERE 2000). In terms of fire protection, information on materials in these phases are the most important, since during them the damage can be minimized to the greatest extent. The point is the thermal decomposition of bonds of its main components such as cellulose, hemicellulose and lignin. When the chemical composition changes, many new products are being created (KAČÍK *et al.* 2017, LUPTÁKOVÁ *et al.* 2018).

Thermal decomposition of cellulose is a complex of chemical reactions that take place at different temperatures. Up to a temperature of 150°C, the bounded water evaporates and changes in cellulose structure (formation of free radicals, lactones, later decarbonylation and formation of CO and CO₂) begin to occur at temperatures above 150°C. Complete degradation of cellulose, especially in its amorphous areas, appears between the temperatures of 180°C and 270°C. Cellulose become more flexible at temperatures above 300°C, and the main reaction is depolymerisation and formation of levoglucosane (SHEN, GU 2009, KUČEROVÁ *et al.* 2012, KAČÍKOVÁ *et al.* 2013). At temperatures above 500°C, levoglucosan begins to transform to combustible gases, CO, CO₂, water and tar substances and char residues (REINPRECHT 2016, KUČEROVÁ *et al.* 2011, MARTINKA *et al.* 2012a, b, 2018).

Most of hemicellulose decomposition take place at temperatures up to 300°C (REINPRECHT 2016, BOONSTRA *et al.* 2007b). Their decomposition is much more complicated mainly due to their structure, which is diverse and therefore their decomposition takes place in stages. The first stage is a partial depolymerization (KO *et al.* 2015, HRČKA *et al.* 2018). In the second stage, they are degraded to monosaccharides and subsequently to volatile products (BOONSTRA *et al.* 2007b). In the second stage, the course of degradation is different, it proceeds so fast that it is not possible to detect intermediates. Thermal stability is impacted significantly by acetyl groups, which are also cleaved (SIVONEN *et al.* 2002, NUOPPONEN *et al.* 2004, WIKBERG, MANUU 2004, JEBRANE *et al.* 2018). The final product of hemicellulose decomposition is methanol, acetic acid, furan and valerolacton (KUČEROVÁ *et al.* 2011).

Changes in lignin during thermal loading are the smallest compared to the other main components of wood because it is the most thermally stable component of phytomass. Lignin degradation begins at relatively lower temperatures, at the same time, new products of its decomposition are formed. At higher temperatures, cross-linking and condensation attains (NUOPPONEN *et al.* 2004, WINDEISEN *et al.* 2007, KUČEROVÁ *et al.* 2016).

Degradation of the main chemical components of wood closely relates to mechanical strength of wood (BOONSTRA *et al.* 2007a, KAČÍKOVÁ *et al.* 2011). Therefore, it is necessary to protect wood from effects of thermal exposure. It is important to pay attention to compliance with valid regulations and standards, especially in the area of fire safety of buildings. Protection of wood materials by e.g. flame retardants helps to meet required time criteria, criteria for load carrying capacity and stability in case of fire. Due to measures provided by flame retardants, the load bearing structures are able to resist effect of fire longer. It is important for the safe evacuation of persons and for the safe intervention of firefighting units (KAFKOVÁ 2006).

Some flame retardants (intumescent retardants Flamgard, Flamgard Transparent, etc.) under thermal load create a foam, which is an insulating layer between material and thermally loaded layer or they support the formation rate of charred layer and thus increase the fire resistance of solid wood.

The thickness and speed of charring is one of the most important fire properties of wood and wood product. (BABRAUSKAS 2005). In assessment of fire spread, the technical standard (Eurocode 5) is the most reliable for analysis the charring depth. To determine the

time of burning and fire intensity, the charring depth is defined according to the standard STN EN 1995-1-2: 2004 as a distance between the outer surface of the original element and the position of the line between the charred layer and the rest of the cross-section. The standard specifies the line of the charred layer of wooden construction as the place where the temperature reaches 300°C. According to FONSECA and BARREIRA (2009), the charred layer is the dividing line between thermally degraded and non-degraded wood, bounded by a black and a brown wood layer and is characterised by the temperature of 300°C. In accordance with WHITE and NORDHEIM (1992), the charred layer corresponds to the temperature of 288°C. Results of the scientific work of FINDORÁK *et al.* (2016) confirms above mentioned statements, i.e. rapid thermal decomposition of wood (in case of short-term exposure) starts just below the temperature of 300°C.

The aim of the paper is to assess the effectiveness of retardant applied to spruce wood at thermal loading. Degradation of wood was assessed through changes in the course of temperatures in material during its thermal loading, by measuring of charred layers, but also by chemical analysis, where changes of the main wood components i.e. extractives, lignin, cellulose and hemicellulose were detected.

MATERIAL AND METHODS

Samples

The samples of spruce wood (*Picea abies* L. Karst.) (harvested in the east part of Slovakia in Dobšiná, trunk diameter approximately of 35 cm, age of 85 years) were cut into the shapes of blocks with the dimensions of 150 × 150 × 1,000 mm (thickness × width × length). The wood surface was treated by 80 grit sandpaper.

The retardant was applied by painting to the air-dry wood (moisture of 8 %) in three coats in a time interval at least of 24 hours, within one week. The overall coating thickness was 500 g/m² in line with the instructions of producer, which is our case 300 g of retardant per sample. The weight of applied retardant was less than 1% of the weight of the test sample.

Used flame retardant

Flamgard

Flamgard flame retardant is produced by Stachema company. The substance contains ammonium phosphates, foaming additives, flame retardants, polymers and additives. In case of fire, substance can create harmful gases and vapours (CO₂, CO, NO_x, P_xO_x, NH₃, vapours of acetic acid (KBÚ, www.stachema.sk).

Radiant heat

Three types of samples were thermal loaded, i.e. one control (untreated) sample and two samples treated by retardant Flamgard.

The source of the radiant heat was a ceramic radiant panel used for model testing of the evaluation of building elements from the fire protection point of view. The source of heat can be characterized by the following data: the dimensions of the radiation zone – 480 × 280 mm, max. performance of the radiation zone – 50.5 kW·m⁻², the total reached temperature of the radiation zone – 935°C. To achieve the requested performance, the heat flow (30.9 kW·m⁻²) needed to supply the body of the radiant with propane at the constant flow of 13 l·hour⁻¹. We placed the support holder 20 cm from the radiation panel on which we placed the thermocouples of type K (Ni-Cr-Ni), which measured the temperature on the surface of the block. We also placed in the same room a second thermocouple of type K which measured the temperature of the environment during the experiments ($t = 25.0 \pm 0.7$ °C).

The first thermocouple (M0.0) was placed on the site, which was directly exposed to the radiant heat from the radiant panel. Another five thermocouples were inserted into drilled holes (75 mm deep below the surface, which is the centre of the sample) on the top side of the wooden block (M1.0 – M5.0) at a distance of 10 mm from each other. Thermocouples on the top side of the sample were covered by mineral wool during the measurement. The last thermocouple was freely placed in the testing laboratory and measured ambient temperature. The samples were gradually placed on the stand in front of the radiation panel (distance 20 cm) and were thermally loaded for 30 and 45 minutes per treated samples, and for 30 minutes per untreated sample. The process was monitored and recorded by digital measurement device (Data logger ALMEMO® 710). The recorded data were then evaluated.



Fig. 1 Emplacement of the thermocouples M 0.0 – M 5.0.

Size and depth of charred area

The measurement was conducted using a laboratory measuring instrument and a digital calliper. Firstly, the length of the charred layer was measured. To measure the depth of the charred layer, it was needed to remove this layer. After removing of the charred layer, the depth was measured in nine predetermined points (starting in the middle of the sample and then continuing at the distance of 100 mm from the centre).

Sampling for the purpose of chemical analysis

Sawdust was needed to determine chemical composition of wood. Two layers were removed by a circular saw. The first one with the thickness up to 20 mm (layer 1) and the second one with the thickness from 20 to 40 mm (layer 2) below the charred layer.

Chemical composition of wood

Samples were disintegrated into sawdust, and fractions in size of 0.5 mm to 1.0 mm were used for the chemical analysis. The extractives content was determined with the use of Soxhlet apparatus with a mixture of ethanol and toluene (2:1) according to ASTM D1107-96 (2007). The lignin content was determined according to SLUITER *et al.* (2012), and the cellulose content was determined according to the method by SEIFERT (1956), and the holocellulose content according to the method by WIESE (1946). Measurements were conducted on four replicates per sample. The results were presented as oven-dry wood percentages.

RESULTS AND DISCUSSION

Temperature changes during thermal loading by radiant heat, depth of charred layer

Fig. 2, 4 and 5 shows temperature changes on particular thermocouples during the thermal loading of untreated sample of spruce wood and samples treated by flame retardant Flamgard.

Based on the course of temperatures in the sample it is possible to determine the thickness of charred layer not only by its measurement but also by determination of time when the critical temperature 300°C was reached (as mentioned above by several authors).

Control sample

Immediately after placing the sample in front of the radiant panel we observed blackening the surface, creation of charred layer, smoke and smouldering. Flame burning occurred in the 19th minute. In Fig. 3, we can observe burning in time of 1140 sec and at the temperature of 489.80°C (M 0.0). Flames were visible from 3rd minute. Burning did not spread to the opposite side of the sample. Nevertheless, we could see higher increase of temperature on thermocouple M 1.0. Sharper increase of the temperature was not recorded on thermocouple M 2.0. On other thermocouples, the temperature increased slowly, however up to a maximum of about 200 °C.

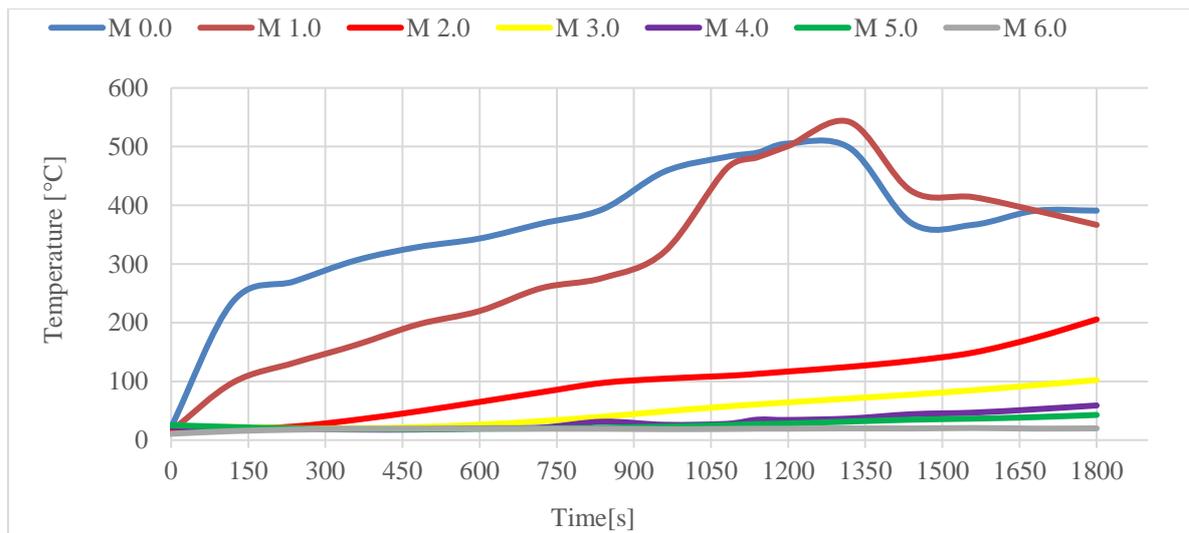


Fig. 2 Temperature changes during thermal loading, control sample (M 0.0, M 1.0, M 2.0, M 3.0, M 4.0, M 5.0, M 6.0 - thermocouples).



Fig. 3 Flame combustion of control sample.

In case of untreated sample, on thermocouple M 1.0, the temperature of 300°C was reached in time of 920 sec which correspond to the thickness of charred layer 10 mm below the thermal loaded surface. On other thermocouples (M2.0 – M5.0), the limit temperature 300°C was not reached in the time interval up to 1800 sec.

The average thickness of charred layer was 15.41 mm, maximum thickness was 18.40 mm and minimum thickness was 10.10 mm (Table 1).

Treated sample, time of thermal loading 30 minutes

After a short time from the beginning of thermal loading, stronger smoke, audible cracking and creation of charred layer were observed. In comparison with the control sample, we can see on Fig. 4, that the temperatures in time of 240 seconds on thermocouple M 1.0 are different (130.0 °C in case of control sample, and 79.3°C in case of sample treated by Flamgard). We can conclude that the retardant protected the sample from the rapid increase of temperature and subsequent ignition. The overall course of temperatures increase on particular thermocouples is shown in Fig. 4.

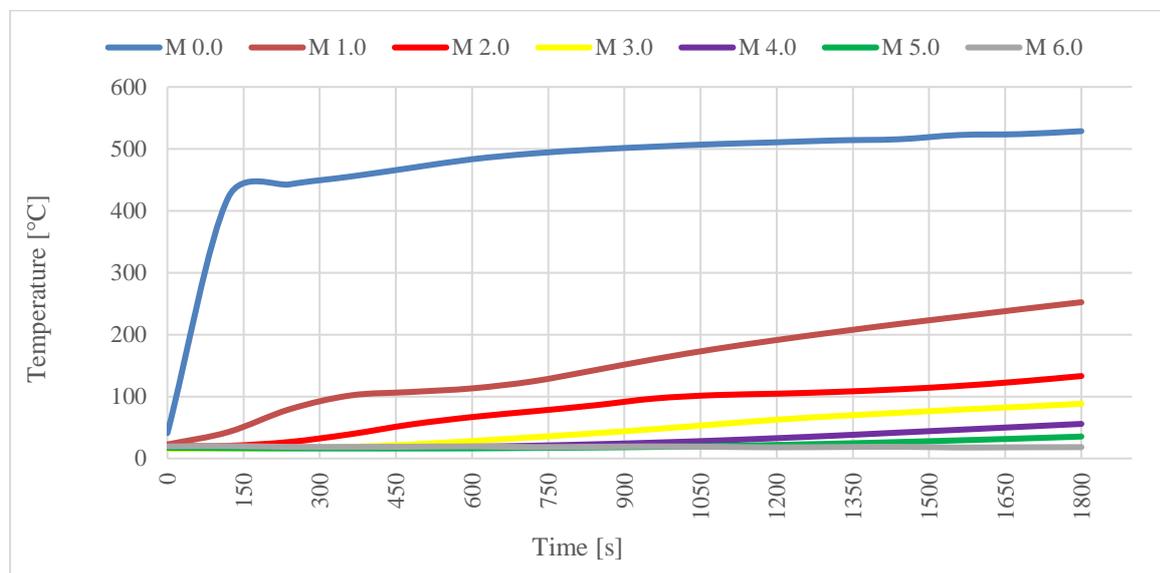


Fig. 4 Temperature changes, treated sample, thermal loading 30 minutes (M 0.0, M 1.0, M 2.0, M 3.0, M 4.0, M 5.0, M 6.0 - thermocouples).

In case of sample treated by retardant Flamgard, thermally loaded for 30 minutes, the limit temperature of 300°C was not reached on any thermocouples (M1.0 – M5.0) (Fig. 4), therefore we can conclude that the retardant protected the sample.

Average thickness of charred layer was 10.03 mm (Table 1), which is approx. 5 mm less than in case of control, untreated sample. Maximum thickness of charred layer was 12.60 mm (18.40 mm in case of untreated sample). Since both samples were exposed to radiation heat for the same time interval, we can conclude that retardant Flamgard increased resistance of spruce wood to its thermal degradation during 30 minutes.

Treated sample, time of thermal loading 45 minutes

The course of the experiment was similar as in case of treated sample thermally loaded for 30 minutes. However, in case of the sample thermally loaded for 45 minutes we could see flameless burning (Fig. 6). Small pieces of charred layer fell off. Due to effects of radiant heat with heat flow 30.9 kW·m⁻² we could also observe marked cracks, especially in weak spots of the sample.

In case of the sample treated by retardant Flamgard, thermally loaded for 45 minutes, the limit temperature of 300°C was not also reached on any thermocouple (M1.0 – M5.0) (Fig. 5). Maximum temperature of 292°C was reached on thermocouple M1.0, in time of 2700 sec from the beginning of thermal loading. Based on that, we can also conclude that the retardant Flamgard protected the sample, only surface charring occurred.

Tab. 1 Thickness of the charred layer of samples.

Treatment	Time of thermal loading (min)	Thickness of charred layer (mm)		
		min	max	average
Control sample	30	10.10	18.40	15.41
Treated sample	30	7.28	12.60	10.03
	45	15.60	31.10	20.04

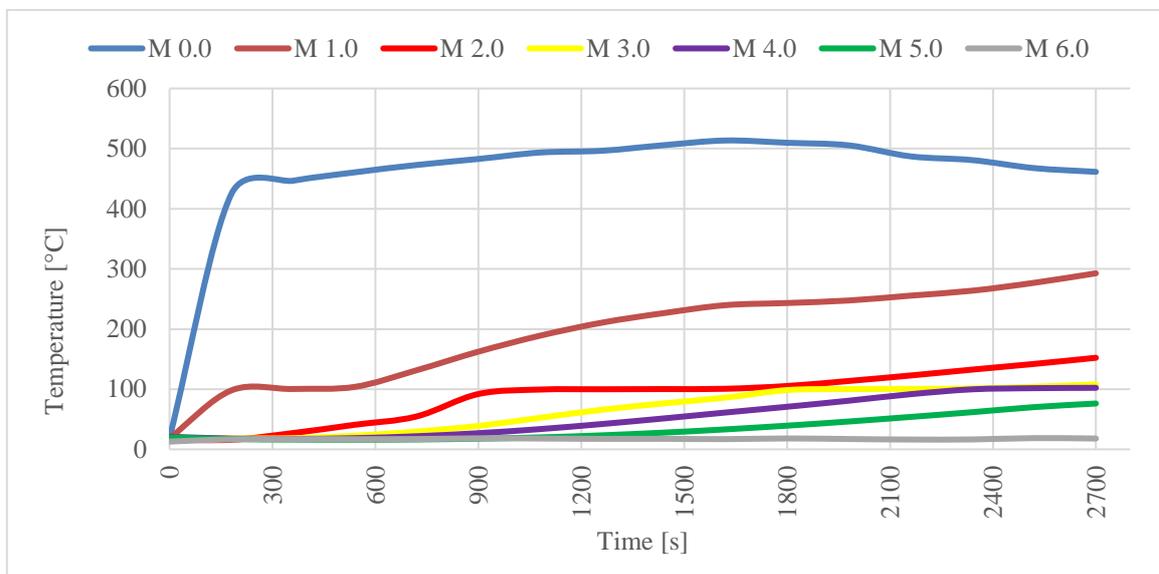


Fig. 5 Temperature changes during thermal stress, threated sample, thermal loading 45 minutes (M 0.0, M 1.0, M 2.0, M 3.0, M 4.0, M 5.0, M 6.0 – thermocouples).



Fig. 6 Flameless burning of sample.

In case of the sample treated by retardant Flamgard, thermally loaded for 45 minutes, the average thickness of charred layer was 20.04 mm, and the maximum thickness of the layer was 31.10 mm (Table 1). When comparing the determination of the thickness of the charred layer using the critical temperature 300°C and manual measurement (in nine points on the surface of the sample), there is a significant deviation among determined values. Similar conclusions can be find in scientific papers by WHITE and TRAN (1996), who tested different tree species at heat flows 15, 25, 35 and 50 kW·m⁻². Their conclusions showed, that the charring rate of wood exposed to a constant external heat flow can be regarded as a linear function of time, however at higher levels of heat flows its behaviour can be non-linear with longer time interval needed to reach a given depth of charring. The charring rate is directly proportional to the ratio of exposure to external heat flow and density. Testing of Nordic spruce samples according to HADVIG (1981) reached charred layer 24–27 mm (at thermal loading for 30 minutes) and 30–32 mm (at thermal loading for 40 minutes), which is comparable with our results in case of untreated samples.

Chemical analysis of wood after thermal loading

The main components of wood include holocellulose (HOL), i.e. cellulose (CEL) and hemicelluloses (HEMI), lignin (L) and extractives (EL).

Table 2 shows chemical composition of original wood sample and wood sample after thermal loading.

Tab. 2 Chemical analysis of wood before and after thermal loading.

Treatment	Time of thermal loading (min)	Layer	EL (%)	L (%)	HOL (%)	CEL (%)	HEMI (%)
Original wood sample	-	-	2.12±0.02	29.12±0.27	78.32±0.73	41.63±0.06	36.69±0.79
Control sample	30	1	3.55±0.13	25.55±0.06	65.11±1.5	35.85±0.45	29.26±1.06
		2	3.24±0.09	26.69±0.04	69.33±0.02	37.62±0.01	31.71±0.02
Treated sample	30	1	2.13±0.09	27.29±0.02	77.25±0.46	45.34±0.86	31.63±0.40
		2	1.92±0.05	28.04±0.24	78.75±0.44	44.16±0.29	34.59±0.73
	45	1	3.20±0.11	27.24±0.04	75.08±0.08	44.38±0.57	30.70±0.65
		2	2.13±0.12	28.57±0.25	77.89±0.32	43.81±0.95	34.08±0.63

During thermal loading of spruce wood occurs to the changes of chemical composition. It is not just about surface changes such as colour or weight loss but also changes in chemical composition of the main components of wood and extractives (KAČÍK *et al.* 2006). It results from chemical analysis (Table 2) that thermal loading increases the percentages of extractives in samples. The amount of extractives is increased by products of macromolecule decomposition of lignin, cellulose and hemicellulose (BOONSTRA *et al.* 2007b, WINDEISEN *et al.* 2009). Lower values can be observed in the second layer of sample, and it can be assumed that there was such considerable degradation compared to the first layer.

Lignin belongs to the most thermally stable components of wood. There were no notable changes during radiant heat of samples. A slight decrease of the proportion of lignin can be observed in all samples compared to the original sample (without thermal loading). We can conclude that the use of retardant Flamgard provided some protection against lignin degradation (decrease of lignin content of treated samples was from 1.89 to 6.46%).

Decrease of the carbohydrates component of wood (holocellulose) is minimum (from 0 to 4.14%) in case of samples treated by retardant. A slight decrease of values can be seen

in a layer immediately below carbonized layer (layer 1). The highest decrease of HOL was in case of control sample, i.e. by 16.87 % (layer 1), and by 11.48% (layer 2). The decrease in the amount of holocellulose relates mainly to degradation of the thermally least stable components of wood i.e. hemicellulose. Similar results for thermal degradation of wood by various means are described by WINDEISEN, WEGENER (2009), and HRČKA *et al.* (2018). According to ZHANG *et al.* (2013), the amount of holocellulose and α -celullose decreases significantly with increasing temperature and duration of thermal loading at temperatures above 160°C, which closely relates to the loss of material weight.

The amount of cellulose in samples treated by retardant was increased. KUČEROVÁ *et al.* (2012) described this phenomenon as a process of charring and crosslinking of cellulose macromolecules. Decrease of this wood component was recorded only in control sample where the proportion of cellulose was degraded by 13.88% (layer 1) and by 9.63% (layer 2).

Hemicelluloses are the most thermally weak components and their degradation begins at relatively low temperatures (BOONSTRA *et al.* 2007 b, KO *et al.* 2015, HRČKA *et al.* 2018, JEBRANE *et al.* 2018). The amount of hemicelluloses in the control sample decreased by 20.25% (layer 1) and by 13.57% (layer 2) compared to the original wood. A decrease in the hemicelluloses content in the samples treated with the preservative is evident, especially in the upper layer, but the degradation of these components did not occur to the same extent as in the untreated sample. Changes in the hemicelluloses content have a significant effect on the strength properties of wood (SWEET, WINANDY 1999, KAČÍKOVÁ *et al.* 2013).

Depending on the type of thermal loading of wood (temperature, time, atmosphere, etc.), there are significant changes in its chemical composition, which is directly related to mechanical (BONSTRA *et al.* 2007a, b, ESTEVES *et al.* 2008, KAČÍKOVÁ *et al.* 2013) and the physical properties of wood (KUČEROVÁ *et al.* 2019).

According to the changes in the proportion of carbohydrates, it can be stated that the flame retarding treatment slowed down the degradation of the main components of wood and its effect lasted also after a long time of exposure to radiant heat source.

CONCLUSIONS

In this study, we investigated the effect of thermal loading by radiant heat source on spruce wood samples treated with a Flamgard retardant. During and after the thermal loading, we evaluated the degree of its charring (extent and depth). We found that once a continuous carbon layer was formed, the degradation of the wood slowed down. This is due to the well-known fact that the carbonized layer itself acts as a flame retardant for specific time. As the temperature on the surface of the sample rose, the coating foamed and increased its volume, creating a kind of protective barrier that slowed down the degradation of the wood.

We compared the results related to the thickness of charring layer by reaching a critical temperature of 300 °C, specified also in Eurocode 5, which was determined by thermocouples placed in the cross section of the sample and further manually measured (at nine places on the sample surface). We found a significant deviation between those values. Retarder Flamgard has a demonstrable wood protective function due to its prohibitive capability to reach a critical temperature of 300 °C, in the depth of 10 mm below the surface of the sample. However, when manually measuring the thickness of the charred layer, it reached a value of 20.04 mm, which means that the degradation of the wood nevertheless occurred at lower temperatures.

This was manifested precisely by monitoring the changes in the chemical components of wood. We performed chemical analyses from two layers of wood. The first was taken to

a depth of 20 mm and the second from 20 to 40 mm below the carbonized layer. The results of chemical analyses showed that by thermal loading of spruce wood:

- There increases the percentage of extractives in the samples. The content of extractives is increased by the decomposition products of the lignin macromolecule and by the carbohydrate components of the wood.
- There were no considerable changes of lignin content (decrease from 1.89 to 6.46%) in the samples treated with the flame retardant. We can therefore conclude that the use of Flamgard retardant provided some protection against lignin degradation.
- The decrease in the proportion of the carbohydrate component (holocellulose) were from 0 to 4.14% in both layers for the samples treated with the flame retardant. The decrease in carbohydrate content was the highest in the control sample (16.87%).
- The content of celluloses in the samples treated with the flame retardant probably increased due to the cross-linking of the cellulose macromolecules caused by thermal loading. A decrease in the cellulose we recorded only in the control sample.
- The amount of hemicelluloses in the control sample was reduced more compared to the original wood. A decrease in these components is also evident in the samples treated with the flame retardant, especially in the upper layer, but not to the same extent as in the control sample.
- Changes in the proportion of carbohydrates showed that the flame retardant slowed down the degradation process of these components of wood and its effect lasted even after a long time of exposure to radiant heat source.

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